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# **MAGNESIUM RICH PRIMER FOR CHROME FREE PROTECTION OF ALUMINUM ALLOYS (Preprint)**

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## **MAGNESIUM RICH PRIMER FOR CHROME FREE**

### **PROTECTION OF ALUMINUM ALLOYS**

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#### **ABSTRACT**

Hexavalent chromium compounds used for corrosion protection are one of the top hazardous waste materials generated by the U.S. Air Force and legislation is in effect to further restrict their use. Magnesium rich primers that utilize sacrificial magnesium metal pigment to cathodically protect aerospace aluminum alloy substrates are a potential alternative to chromated primers. This material has proven to be particularly effective as part of a completely chromate-free coating system in which a non film forming surface treatment and an Advanced Performance Coating (APC) grade topcoat are utilized. Samples using the latest advanced formulations show excellent corrosion protection of scribed AA2024-T3 panels in both ASTM B 117 and outdoor exposure at Daytona Beach, FL. Despite initial concerns regarding the reactivity of the magnesium metal pigment being used, the flammability and handling characteristics have not shown any potential problems to date. Transitioning a new class of corrosion protective primer coating such as this requires more testing than normal. The current Air Force plan involves qualification to a “system level” coating specification, MIL-PRF-32239. In addition, simulated lap joints with various fasteners specific to the target aircraft will be evaluated, along with compatibility on alternative substrates and evaluation of coating reparability characteristics.

Keywords: magnesium rich primer, cathodic protection, aluminum corrosion, sacrificial anode, chrome-free

#### **INTRODUCTION**

##### **Background**

Currently approved coating systems for nearly all aluminum alloy DoD assets utilize Cr(VI) compounds in both the surface treatment and primer coating layers. The Occupational Safety and Health Organization (OSHA) classifies hexavalent chromium compounds as toxic and carcinogenic. A

complete toxicological review is available from the Environmental Protection Agency (EPA) which strictly regulates Cr(VI) emissions, contamination, and disposal.<sup>1</sup> Use of chromates by the DoD in paint operations incurs significant direct and indirect cost burdens for waste stream disposal, EPA and OSHA compliance, site remediation, and personnel exposure liability. The total cost of corrosion to the entire DoD is already estimated at \$10-20 billion per year.<sup>2,3</sup> Therefore, little or no reduction in the corrosion protection performance of non-chrome technologies can be tolerated, thus further increasing costs.

In addition, a recently passed rule change by OSHA (29 CFR Parts 1910, 1915, et al.; passed on 28 FEB 2006)<sup>4</sup> establishes an 8-hour time-weighted average (TWA) personal exposure limit (PEL) of 5 micrograms of Cr(VI) per cubic meter of air ( $5 \mu\text{g}/\text{m}^3$ ), which is over an order of magnitude reduction from the previous PEL of  $52 \mu\text{g}/\text{m}^3$ . Aircraft finish operations are high volume users of hexavalent chromium materials and no current material substitution exists. Therefore, this sector has been given a special higher compliance limit of  $25 \mu\text{g}/\text{m}^3$ . A summary of current OSHA limits for all chromium valences is provided in TABLE 1. The final rule also contains ancillary provisions for worker protection such as requirements for exposure determination, preferred exposure control methods, respiratory protection, protective clothing and equipment, hygiene areas and practices, medical surveillance, recordkeeping, and start-up dates that include four years for the implementation of engineering controls to meet the PEL. Since additional restrictions on the emissions and disposal of toxic chromium compounds are expected from the EPA in future years regarding both solid waste and wastewater effluents, direct DoD costs associated with continued use of Cr(VI) compounds are expected to increase significantly.

**TABLE 1**

**SUMMARY OF OSHA STANDARDS RESULTING FROM 28 FEB 2006 RULE CHANGE**

Chromium (II) compounds	$500.0 \mu\text{g}/\text{m}^3$
Chromium (III) compounds	$500.0 \mu\text{g}/\text{m}^3$
Chromium (VI) compounds (chromates)	$5.0 \mu\text{g}/\text{m}^3$ (previously 52.0) $25.0 \mu\text{g}/\text{m}^3$ for aircraft finishes (previously 52.0)
Chromic acid	$5.0 \mu\text{g}/\text{m}^3$ (previously 52.0)
Chromium metal and insoluble salts	$500.0 \mu\text{g}/\text{m}^3$

Although research and development into non-chrome technologies by academia, industry, and government laboratories has progressed appreciably over the past fifteen years, the lack of an effective benign replacement has resulted in the continued use of these materials. Many of these alternatives being used still rely upon the presence of chromium (III) or (VI) present somewhere in the total coating system (i.e., either the primer or surface treatment). Furthermore, none of these systems to date have matched or outperformed the corrosion protection capabilities of the current chromate conversion coating/strontium chromate pigmented primer combinations used on most aluminum structures. However, recent novel developments have been made in academia<sup>5</sup> which has shown promise in developing a Cr-free coating system based on *cathodic protection* of the substrate rather than conventional use of passivating corrosion inhibitors (e.g., chromates, molybdates, and other rare earth compounds). The cathodic protection is realized through the use of a magnesium rich (Mg-rich) primer, which is analogous to a zinc rich primer used to protect steel substrates. As the name suggests, a Mg-rich primer is a coating which contains magnesium metal powder pigment as a sacrificial anode.

### Technology Description

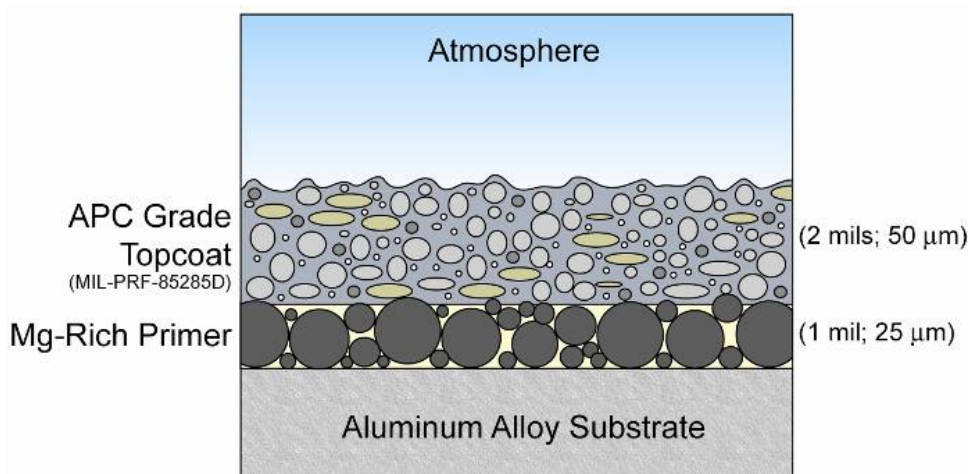
Magnesium is more active (i.e., anodic) in the galvanic series than aluminum and its alloying constituents. Therefore, it has the capacity to cathodically protect aluminum substrates. When primer

coatings are formulated with magnesium metallic pigments at a high enough volume concentration so that nearly all of the particles are in contact with each other, and, when the primer is in direct electrical contact with the aluminum substrate, the Mg pigment will corrode sacrificially in place of the aluminum alloy. This mode of corrosion protection of aluminum alloys is a completely different approach than through the use of inhibitor pigments and can facilitate coating systems (i.e., surface treatment, primer, topcoat) that are totally free of chrome (in any valence) or other heavy metal compounds. While the concept of cathodic protection itself is not novel, the concept to use Mg as a pigment to protect aluminum was conceived by Bierwagen and Nanna. They also generated the first prototype films and demonstrated that cathodic protection of aluminum was possible by having scribed panels pass several thousand hours in ASTM B 117 salt fog exposure.

The performance of Mg-rich primers versus conventional inhibitor based primers as part of a complete coating system is notably different as well. While strontium chromate pigmented primers still perform well over many non-chromate surface treatments, the best performance is generally obtained with the use of chromated conversion coatings, (e.g., Alodine 1200™). This is particularly true for non-chromate primers which often rely upon the chromated conversion coating (CCC) to obtain reasonable results. To date, combinations of non-chrome primers and non-chrome surface treatments have not produced the desired level of corrosion protection. Currently there are no aluminum skinned military aircraft which have authorization to use such completely chromate-free coating systems. Since Mg-rich primers function via cathodic protection, satisfactory performance actually requires that no electrically insulating surface treatment layer be present. This effectively eliminates the need for a conversion coating surface treatment and ensures that the total coating system is Cr and heavy metal free. Nevertheless, one of the functions of a surface treatment is to ensure proper substrate decontamination and paint adhesion. There are some non-film forming surface treatments available (e.g., PreKote™) to prepare bare aluminum substrates for painting. These products work exceptionally well with Mg-rich primers because they do not leave an insulating film layer and facilitate better adhesion of the primer to the substrate.

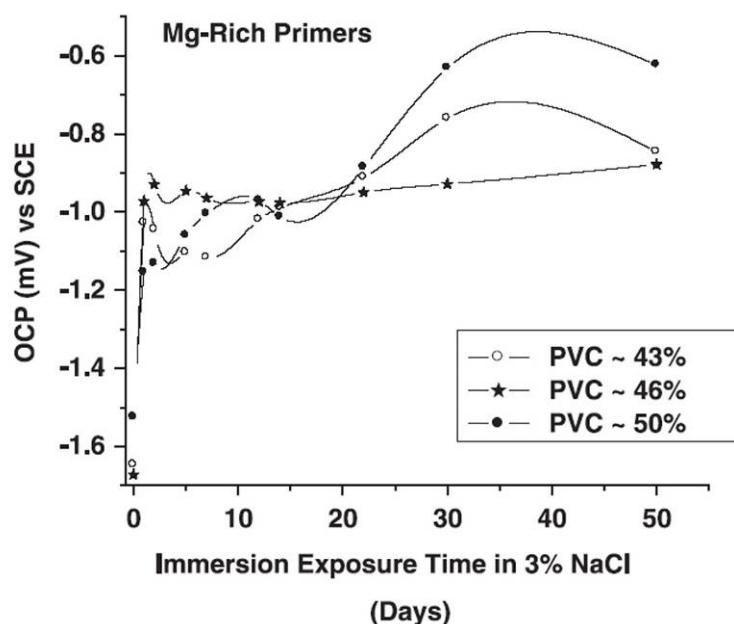
Another notable performance difference between Mg-rich primers and conventional primers when evaluated as a coating system is the effect of topcoat choice. Over the last decade, the use of Advanced Performance Coating (APC) grade aircraft topcoats by the Air Force has grown tremendously due to their superior weathering and cleanability characteristics. However, the performance of scribed panels in ASTM B 117 of APC topcoat over conventional primers has consistently shown worse results than those when a standard MIL-PRF-85285D topcoat is used. A potential explanation of these results may be due to the fact that most APC grade topcoats have much better barrier properties. The reduced water diffusion through the topcoat may not sufficiently dissolve the corrosion inhibitors in the primer to allow enough corrosion *control* (i.e., passivation) to occur. This trend tends to be more prevalent in non-chromate primers versus chromate primers. It is unclear yet whether this trend can be extrapolated to actual in-service performance. For unscribed/undamaged coatings, corrosion *prevention* is always better with increasing topcoat barrier properties. Thus, a suitable balance between corrosion *prevention* and corrosion *control* must be found when conventional inhibitor based primers are used. Fortunately, Mg-rich primers always function better in both corrosion *prevention* and *control* aspects when higher barrier APC grade topcoats are used. This stems from the fact that there are no inhibitor pigments in the primer which need to dissolve and migrate in an aqueous environment.

The preferred coating system stack-up that relies on Mg-rich primer for corrosion control would involve only three processes: 1. the aluminum substrate must be properly cleaned and prepared for subsequent painting (e.g., use of PreKote) to enhance adhesion; 2. Mg-rich primer is applied directly to the prepared aluminum substrate at a dry film thickness of ~1 mil; 3. A high barrier property APC grade topcoat is used to enhance corrosion prevention properties of the coating system. A schematic cross-section of a coating system which utilizes a Mg-rich primer is provided in FIGURE 1.



**FIGURE 1 – Schematic cross-section of a magnesium rich primer based coating system for corrosion protection of aluminum alloys.**

The presence of a cathodic corrosion protection mechanism can be verified through the use of a potentiodynamic scan (PDS) measurement to obtain the open circuit potential (OCP). The OCP values of bare AA2024-T3 and Mg are about  $-0.7 V_{SCE}$  and  $-1.6 V_{SCE}$ , respectively in 0.1M NaCl electrolyte. When a properly formulated Mg-rich primer is applied to a AA2024-T3 substrate and this measurement is made, the resultant mixed potential ranges from  $-1.2$  to  $-0.9 V_{SCE}$  (FIGURE 2). As long as the resultant mixed potential of the system is well below that of the substrate, the substrate should be cathodically protected from corrosion.



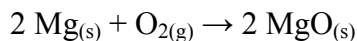
**FIGURE 2 – Open circuit potential of a series of Mg-rich primers over AA2024-T3 substrate, from Bierwagen and Nanna.**

### Reactions of Pure Mg Metal

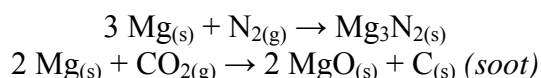
One of the reasons why Mg was not historically explored in great detail as a sacrificial anode pigment in coatings for aluminum substrates is the fact that Mg is relatively high in the activity series of the elements. Mg is a member of the Group IIA elements, or alkaline earth metals, of the periodic table. Within the Group IIA elements, the reactivity and softness increase with elements lower in the column.

Only Beryllium (Be) and Mg are stable in air; the others (Ca, Sr, Ba, Ra) are too reactive and must be stored in an oxygen free and moisture free environment.

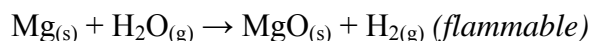
Flammability: Pure Mg metal is highly flammable and burns vigorously in air, forming magnesium oxide. While it is easy to ignite when powdered or shaved into thin strips (i.e, high surface area), it is difficult to ignite as a bulk solid. The reaction in air proceeds as:



Mg fires present a very unique hazard and must be extinguished using a Class D Type 1 fire extinguisher only. Once ignited, they are capable of burning in both a nitrogen gas and carbon dioxide gas environment. This renders many standard fire extinguishers useless. The reactions proceed as:



Using water to extinguish a magnesium fire is never recommended under any circumstances since it literally adds fuel to the fire. This same reaction can occur when steam is in direct contact with Mg, and can cause Mg to subsequently ignite. The reaction proceeds as:



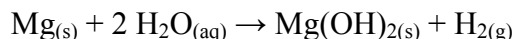
Despite the reactive nature of Mg, in practice, the handling and processing of Mg based materials is relatively safe and industrial accidents are rare. The potential flammability of Mg-rich primer coatings in the manufacturing environment and in both the wet and dry film forms was of concern at the beginning of the development process. The greatest concern was the safety in handling of the bulk magnesium powder, which would only occur at the pigment manufacturing facility and potentially at the coating formulation facility. Applicators and end users of Mg-rich primer would never be exposed to bulk/uncoated magnesium powder. Fortunately, the magnesium industry already produces bulk Mg powder for a variety of other industrial applications and safety practices have already been established. Once produced, the Mg powder is relatively stable towards handling because of the presence of a thin oxide layer (~200 nm), which passivates the surface. The powder does not react quickly upon exposure to room temperature water and does not show signs of violent ignition when directly exposed to flame. Nevertheless, a preferred method of handling the powder by the coating formulator would be as received in a resin-solvent slurry supplied from the powder manufacturer.

The flammability of cured Mg-rich primer films on aluminum substrates have not shown any additional hazard or flame spreading rates as compared to conventional primer coatings. This is most likely due to the fact that the powder is encapsulated in a polymeric resin which limits the exposed Mg surface area and the total mass (i.e., fuel capacity) of Mg is rather small in a 1.0 mil dry film. A full fire prevention and control assessment regarding use of Mg-rich primer for DoD aerospace applications is planned. This activity should cover all aspects of handling the coating including storage, application, on aircraft service, removal, and disposal.

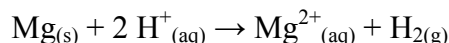
Aqueous Reactions: The presence of Mg powder in a primer film lends itself to a variety of reactions with environmental species under ambient conditions. As previously mentioned, Mg metal will react with steam to form flammable hydrogen gas. However, when pure Mg metal is in contact with ambient liquid water, it does not react to any significant extent. This is in part because the excess of water present facilitates the formation of a nearly insoluble magnesium hydroxide reaction product, which



passivates the Mg surface, protecting the underlying Mg from further reacting. Since the Mg powder used as a pigment already has a passivating MgO layer present, the reaction is even less pronounced.



The presence of an acidic environment due to chemical exposure, acid rain, exhaust plumes from ships or industrial plants, or other scenarios open up the potential reaction of Mg with an acid. The reaction proceeds readily and typically results in the formation of a soluble salt and hydrogen gas. The net ionic equation is represented as:

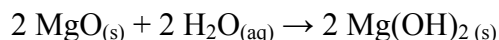


It is important to note that under these conditions, there is no formation of a passivating layer. The Mg metal can be dissolved away since the product is a soluble salt. In contrast to acids, magnesium metal does not react with dilute aqueous alkalis.

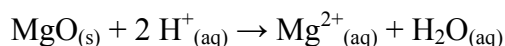
### Reactions of Mg Compounds

The primary Mg compounds of interest are magnesium oxide (MgO) and magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) since they are the species which would be present on the pigment surface or as the by-product of cathodic protection of the substrate. A potentially important aspect of these compounds is their density relative to Mg metal. MgO and  $\text{Mg}(\text{OH})_2$  have densities of 3.60 and 2.37 g/cm<sup>3</sup>, respectively. Both of these compounds are unique in that their density is actually greater than Mg metal (1.74 g/cm<sup>3</sup>). The formation of hydrates with these compounds would no doubt reduce their effective densities. However, compared to zinc rich primers for steel substrates, the Mg sacrificial corrosion products would not induce added physical stress into the coating through volume expansion.

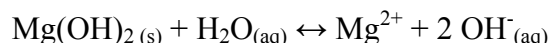
MgO is a stable compound which does not have direct solubility in water, but will react with water to form  $\text{Mg}(\text{OH})_2$ , which is nearly insoluble and helps passivate further MgO surface reaction with water.



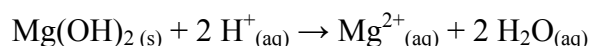
MgO can act as a base with direct reaction toward acids, effectively neutralizing the acid by forming a soluble magnesium salt and water. Unlike reaction with Mg metal, no hydrogen gas is generated during this process. The net ionic equation is:



$\text{Mg}(\text{OH})_2$  is a relatively weak base and is only sparingly soluble in water. The  $K_{sp}$  for  $\text{Mg}(\text{OH})_2$  is only  $5.6 \times 10^{-12}$  according to the CRC handbook.<sup>6</sup> This dissolution in water to generate hydroxyl anions proceeds as:

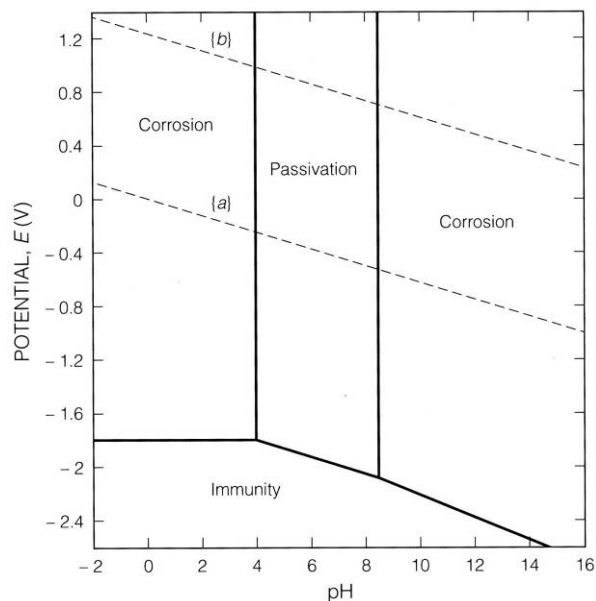


And the net ionic reaction to neutralize an acid and form a soluble Mg salt is:

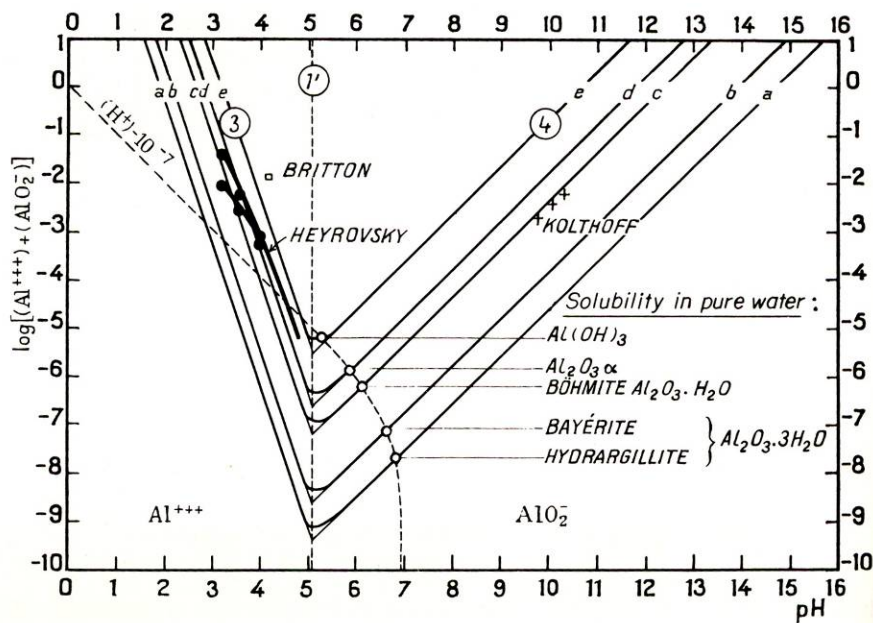


$\text{Mg}(\text{OH})_2$  is an excellent mild base for safe neutralization of acids. In fact, it is commonly referred to as “milk of magnesia” when suspended in water and used as a medicinal antacid.

It becomes evident based on the properties of these compounds that the use of a Mg-rich primer would result in a local coating environment with an acid neutralizing capability. Since either compound has such poor solubility in water, the local pH under a neutral wet environment would not be raised to any significant amount. These compounds would buffer the local environment to near neutrality (i.e., pH = 7). When looking at the Pourbaix diagram for aluminum (FIGURE 3), as well as the pH dependence on the solubility of aluminum oxide and its hydrates (FIGURE 4), one can't help but wonder if the ability to maintain a local pH near neutrality is an additional mechanism present in the corrosion protection of aluminum alloys by Mg-rich primers. This factor could help stabilize the presence of a passivating layer on the alloy surface.



**FIGURE 3 – Aluminum Pourbaix diagram from Jones<sup>7</sup> (pg. 53), which shows the pH dependence on passivation.**



**FIGURE 4 – Solubility of aluminum oxide and its hydrates as a function of pH.<sup>8</sup>**

## QUALIFICATION AND TRANSITION PLAN

The preliminary results generated via the academic versions of Mg-rich primer formulas were very encouraging, particularly since it is a completely Cr-free coating system. This prompted the Air Force and OSD-ATL Corrosion Policy and Oversight office to execute a program with the intent to develop a Mg-rich primer that would meet all of the demanding requirements for DoD aerospace applications, not just corrosion protection alone. This program involved teaming with a major aerospace coating company (Akzo-Nobel Aerospace Coatings, Waukegan, IL) licensed to use the technology to develop an advanced formulation that was capable of meeting the MIL-SPEC requirements as well as critical performance factors not covered under MIL-SPECS but essential to the transition of a new aerospace coating. This program also included two key early performance screening tests. The first was evaluation of Mg-rich primer over a Simulated Aircraft Structure (SAS). The second was performance at an aggressive outdoor exposure location (Battelle, Daytona Beach, FL). Qualification of the resultant Mg-rich primer to MIL-PRF-32239 is currently being performed through an Environmental Security Technology Certification Program (ESTCP) funded project. This effort will also include an in-service flight demonstration on at least two aircraft.

### **Simulated Aircraft Structure Evaluation**

The product development phase performed by the aerospace coating company resulted in a “Generation 1” version of Mg-rich primer that was expected to meet most of the desired performance properties. Since multiple conventional panel tests were already performed in ASTM B 117, the robustness of this first generation primer was evaluated using Simulated Aircraft Structure (SAS) boxes to help identify any compatibility concerns and help guide future formulations to enhance performance.

The SAS boxes were intended to simulate an aircraft wing box and were fabricated out of AA2024-T3 skin plates on the top and bottom and AA7075-T6 on the sides. The top surface panels have several columns of different fasteners present to check for compatibility, which include: Steel Jo-Bolt, Ni/Steel Blind Rivet, Aluminum Blind Rivet, Aluminum HI-LOK<sup>®</sup>, and Steel HI-LOK<sup>®</sup>. Each fastener was “dry” installed (i.e., without sealant) to promote corrosion and represent a worst case scenario. The outer perimeters of the top surface panels were fastened to the edges with steel screws. Copper sulfate solution was also applied to this interface to intentionally initiate corrosion and assess the ability of the coating system to actively suppress corrosion growth. The coating systems used on these SAS boxes were chosen to simulate a refinishing operation, which means that the interiors were prepared with a conventional chromate coating system to simulate that of existing aircraft. The outer mold line coating systems included a chromate control, and various surface treatments in combination with the “Generation 1” Mg-rich primer and APC grade topcoat. The surface treatments included an MEK wipe only, a non-Cr surface preparation product (Pantheon PreKote<sup>™</sup>), and a sol-gel surface treatment (AC Tech AC-131<sup>™</sup>). Alodine 1200 surface treatment was also included to assess the robustness of the Mg-rich primer over residual Alodine that may be present in aircraft refinishing operations. The SAS boxes were evaluated for 2,000 hrs. in ASTM B 117 salt fog.



**a.**



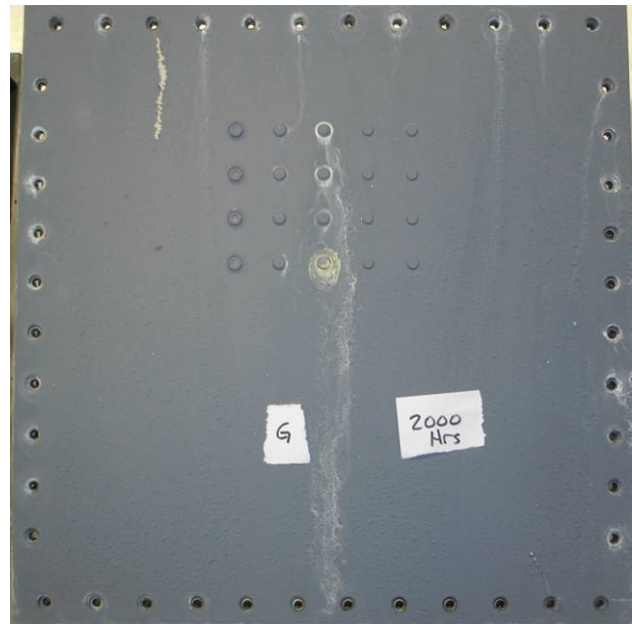
**b.**

**FIGURE 5 – a.) SAS box surface panel with each column of different fasteners identified (A: Steel Jo-Bolt, B: Ni/Steel Blind Rivet, C: Aluminum Blind Rivet, D: Aluminum HI-LOK<sup>®</sup>, E: Steel HI-LOK<sup>®</sup>), and b.) SAS boxes being evaluated in ASTM B 117 salt fog.**

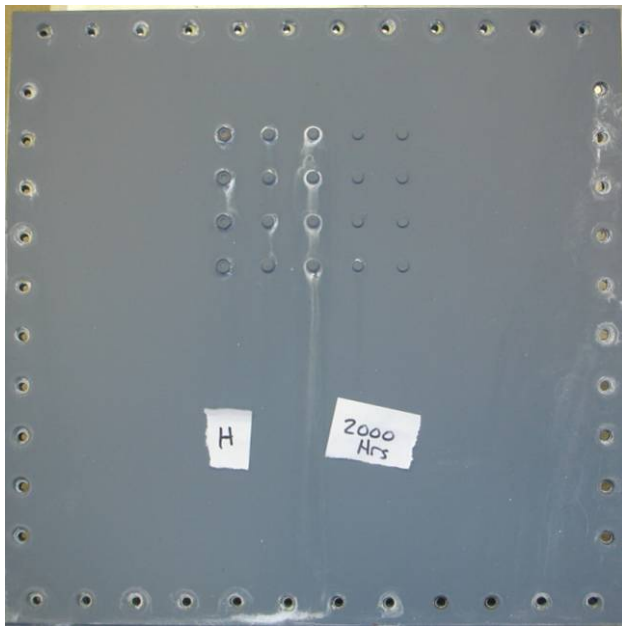
The results of the SAS box evaluation using the “Generation 1” Mg-rich primer suggested that the best performing system was the one which used the non-Cr surface preparation material (PreKote<sup>™</sup>), which performed similarly to the full chromated control. Photos of the samples after 2,000 hrs. ASTM B 117 exposure are provided in FIGURES FIGURE 6 through FIGURE 10:



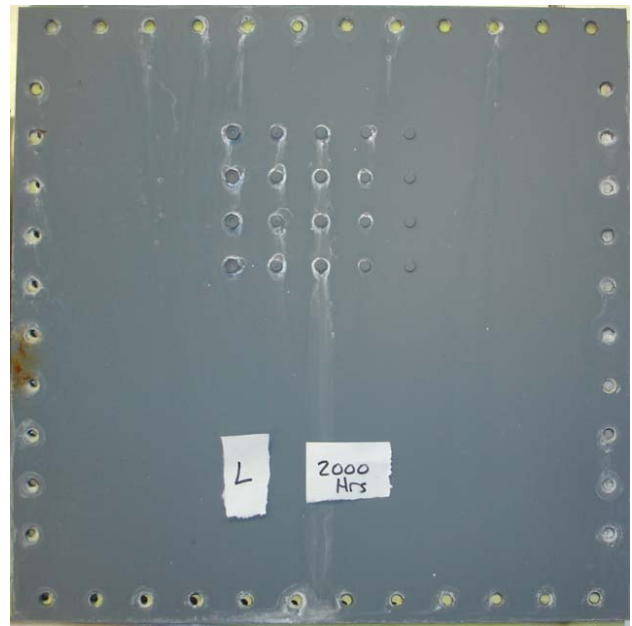
**FIGURE 6 – Full chromated control; corrosion mostly around aluminum blind rivets, some corrosion around Jo-Bolt and Ni/Steel blind rivet; no blistering in the field.**



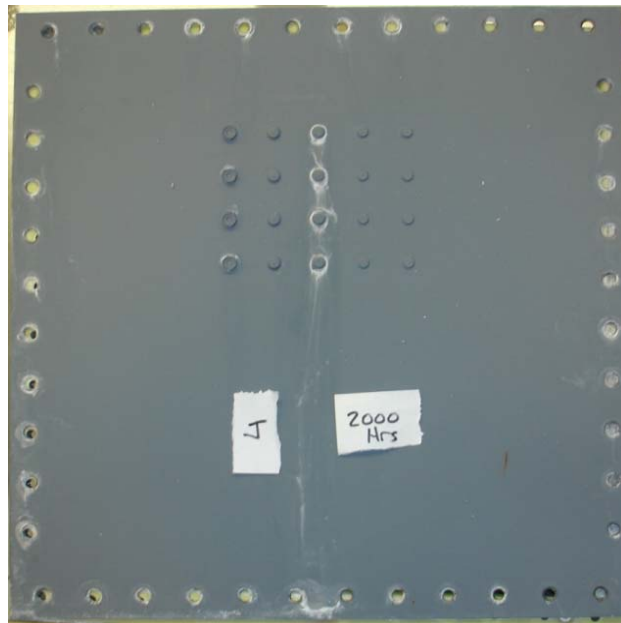
**FIGURE 7 – Mg-rich primer with Alodine surface treatment; some corrosion around aluminum blind rivets; some blistering in the field and slight adhesion reduction.**



**FIGURE 8 – Mg-rich primer direct to substrate with MEK wipe only; some corrosion around aluminum blind rivets and Jo-Bolt; no blistering in the field.**



**FIGURE 9 – Mg-rich primer with AC-131 surface treatment; some corrosion on nearly all fasteners; multiple blistering in the field.**



**FIGURE 10 – Mg-rich primer with Pre-Kote surface treatment; some corrosion around aluminum blind rivets; no blistering in the field.**

The performance of the “Generation 1” Mg-rich primer in the SAS box evaluation validated that performance is better when the primer has direct intimate contact with the substrate. The presence of an insulating surface treatment, such as sol-gel or Alodine, does not allow full electrochemical interaction between the substrate and Mg pigment. These results also helped to guide development of a subsequent “Generation 2” Mg-rich primer formulation that has even greater corrosion protection capability and robustness over substrates which may have small amounts of residual Alodine present. The performance advantages of the “Generation 2” formula are clearly evident in FIGURE 11, which shows a comparison



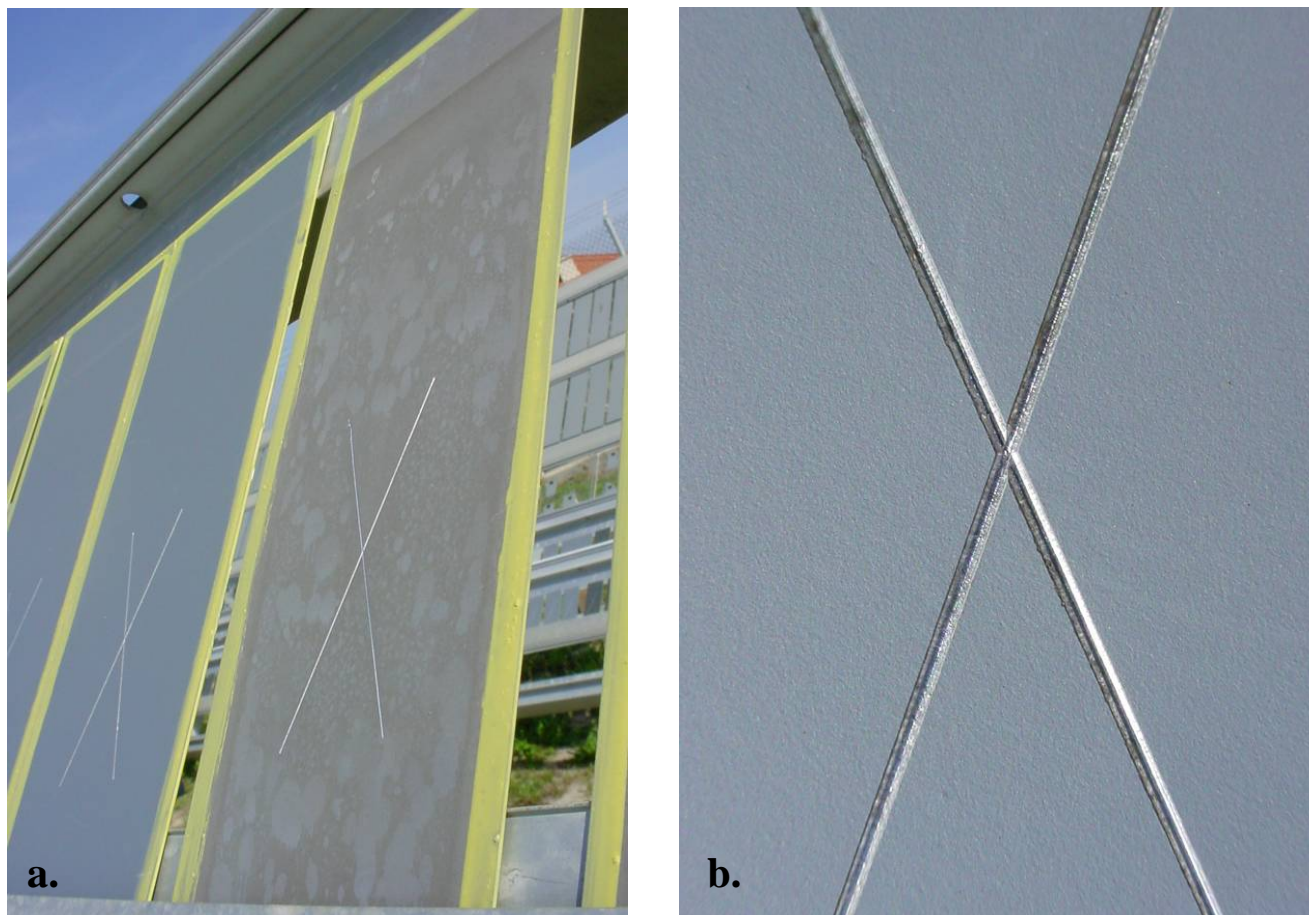
against a chromate control standard as well as the “Generation 1” formulation. The “Generation 2” formulation has been chosen for all future testing. It is VOC compliant at 340g/L, has excellent application characteristics, and has been tinted green to facilitate better contrast ratio for painters to judge wet film thickness.



**FIGURE 11 – Comparison between chromate control (left), Generation 1 Mg-rich (middle), and Generation 2 Mg-rich (right) primers after 2,000 hrs. of ASTM B117 exposure. All systems are on AA2024-T3 and used a non-Cr surface preparation method (PreKote™) and APC grade topcoat (Aerodur 5000™).**

### Outdoor Exposure Evaluation

Due to the sometimes large disparity between accelerated laboratory corrosion testing and outdoor field performance, a series of samples were generated to evaluate the performance of the Mg-rich primer at Battelle’s Daytona Beach, FL test site. The sample matrix includes both Generation 1 and Generation 2 Mg-rich primer formulations over a variety of surface treatments. These surface treatments include: direct to metal (abrade and isopropanol wipe), Alodine 1200, Alodine 5200 (non-Cr), Alodine 5900 (tri-valent Cr), and PreKote. Nearly all samples were topcoated with an APC grade MIL-PRF-85285D in Color 36173 (Aerodur 5000™). While not recommended for actual use, the remainder was left untopcoated with direct exposure of the Mg-rich primer epoxy resin to damaging UV sunlight. In addition, positive full chromate controls and negative blank controls (no inhibitor in the primer) were included for reference. Thus far, only the negative controls are showing any signs of corrosion activity.



**FIGURE 12 – Photos of the “Generation 2” Mg-rich primer after 4 months exposure at Daytona Beach, FL. The panel on the right in (a.) is a sample without a topcoat, which is still showing corrosion protection despite direct exposure to UV and no topcoat barrier properties. Thus far, none of the Mg-rich primer samples show any corrosion activity. (b.) Close-up view of the scribe on a Mg-rich primer direct to metal sample.**

### **Qualification & Flight Demonstration Plan**

The level of testing required to fully transition a new coating to actual field use requires significantly more than those identified in a MIL-SPEC. This is particularly true when qualifying a primer to MIL-PRF-23377J, which does not require the presence of a topcoat nor does it specify compatibility with a particular topcoat product. To alleviate these concerns, the Air Force has developed a new “system level” coating specification, MIL-PRF-32239, which evaluates the performance of an entire coating system, resulting in qualification of a set of compatible coating products. This eliminates the potential for mixing and matching incompatible surface treatments, primers, and topcoats in service. However, MIL-PRF-32239 alone usually does not cover all of the nuances involved in providing enough data for a weapon system corrosion manager to permit a flight demonstration on their asset. Due to these factors, a comprehensive qualification test matrix was generated that includes qualification to MIL-PRF-32239, lap joint evaluations with various fasteners, reparability, performance on specialty substrates, and post-salt fog PATTI adhesion. The target weapon systems for future flight demonstration are C-130 and F-16 aircraft. Since performance over PreKote™ has shown the greatest promise thus far and this product is already widely used at Ogden Air Logistics Center (OO-ALC), the aircraft chosen were those being supported at that location. This reduces the logistical footprint of integrating the Mg-rich primer

since no part of the painting operation would need to be altered. The Mg-rich primer would simply be substituted for the current chromate primer.

This test matrix actually seeks to qualify five different Mg-rich primer based coating systems to MIL-PRF-32239. These are systems E through I in TABLE 2. This matrix also includes four control coating systems as well (A through D).

**TABLE 2**

<b>ESTCP Mg-Rich Primer Qualification Matrix</b>							
	System	Cleaning	Pre-treatment/Conversion Coat	Primer	Special	Secondary Primer	Topcoat
A	WR-ALC C-130 Control	Standard CTIO De-ox and Alkaline Wash	Alodine 1200S MIL-C-5541	Deft 02-Y-40 MIL-PRF-23377	N/A	N/A	Deft 99-GY-001 MIL-PRF-85285
B	OO-ALC F-16 & C-130 Standard Control		PreKote	PRC CA7233 MIL-PRF-23377	N/A	N/A	PRC 9311 MIL-PRF-85285
C	OO-ALC F-16 Gem Control		PreKote	PRC CA7233 MIL-PRF-23377	N/A	N/A	Deft F-16 Specific Topcoat
D	OO-ALC F-16 Mud Control		PreKote	PRC CA7233 MIL-PRF-23377	Deft F-16 Specialty	PRC CA7233 MIL-PRF-23377	Deft F-16 Specific Topcoat
E	MAG1	Standard CTIO De-ox and Alkaline Wash	PreKote	ANAC XP455-30 Mg-Rich Primer	N/A	N/A	ANAC Aerodur 5000 MIL-PRF-85285
F	MAG2				N/A	N/A	Deft 99-GY-001 MIL-PRF-85285
G	MAG3				N/A	N/A	PRC 9311 MIL-PRF-85285
H	MAG4				N/A	N/A	Deft F-16 Specific Topcoat
I	MAG5				Deft F-16 Specialty	ANAC XP455-30 Mg-Rich Primer	Deft F-16 Specific Topcoat

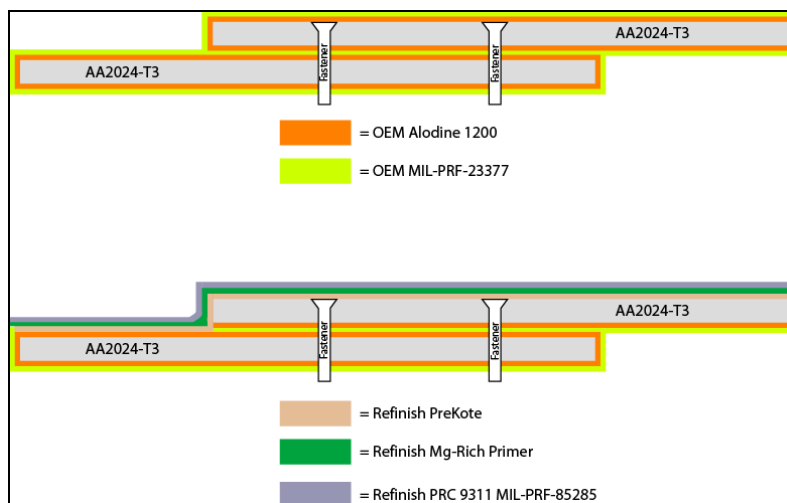
In addition to MIL-PRF-32239 testing, tests will be performed in duplicate over lap joint panels fastened together with various fasteners. Four types of fasteners most commonly used on F-16 aircraft are listed in TABLE 3.

**TABLE 3**  
**COMMON F-16 FASTENERS**

	Fastener Type	Description
F1	MS20426	2117 Aluminum Solid Conventional Rivet
F2	NAS1436H	Pull Type Alloy Steel Stump Lockbolt
F3	MS90353	ASTM-A-331 Sleeve and Pin, 4130 Lock Alloy Steel Blink Huck
F4	NAS1580	4340 Alloy Steel Bolt

Each coupon will be AA2024-T3 bare 3" x 6" x 0.063" and will contain four fasteners of one type. A modified X-scribe will be used and pass through the fasteners. Spacing between the fasteners will be approximately 2" apart on the horizontal and 1" apart on the vertical. The coupons to be fastened together will be AA2024-T3 Bare aluminum coated with Alodine 1200S and chromated primer, to represent an OEM aircraft paint finish. The coupons will be fastened together and the surface of the assemblies that represent the outer mold-line of an aircraft will be chemically stripped. The System G (MAG3) coating system will be applied to the outer mold-line side simulating a refinish application. System B (OO-ALC Standard Control) will be applied to separate coupons to be used as a refinish control. FIGURE 13 depicts the cross-section of the lap joint panel configurations.





**FIGURE 13 – Side view schematic of both the OEM and refinish lap joint panel evaluation setup.**

These coupons will be exposed to salt spray per ASTM B 117 for a minimum of 2,000 hours. The tests will be performed in triplicate. Three assemblies will be X-scribed over the fasteners, three assemblies will have the coating “bridge” broken around the fasteners when possible (fasteners F2 and F4), and the last three assemblies will be exposed with no damage to the coatings.

The reparability of the Mg-rich primer coating will be evaluated by preparing 12” x 12” x 0.032” AA2024-T3 bare aluminum panels with both systems B and G from TABLE 2 as baseline coatings. The repair systems chosen will be the same systems to evaluate all possible combinations of mixing and matching these two different classes of coatings. The panels will be repaired after the coating system is sanded according to FIGURE 14. After sanding, the respective panels will be repaired with the repair coating systems. The panels will be tested with the crosshatch adhesion method over the different interfaces found on the panel with emphasis on the “Untouched to Feathered” and “Feathered to Bare Metal”.



**FIGURE 14 – Schematic of the 12”x12” panel used for evaluating the reparability of the Mg-rich primer coating system.**

The following specialty substrates identified in TABLE 4 will be evaluated for either adhesion, corrosion resistance, or both. Only coating System E (MAG1) from TABLE 2 will be evaluated unless another coating system is identified which performs noticeably better due to an alternative topcoat.

**TABLE 4**  
**SPECIALTY SUBSTRATE MATRIX**

	3"x6" panels				
	Graphite Epoxy	Fiberglass Epoxy	2219-T87 Bare	2195-T8M4 Bare	6061-T6 Bare
<b>Total Number of Coupons Required =</b>	<b>12</b>	<b>9</b>	<b>3</b>	<b>3</b>	<b>3</b>
Wet Tape Adhesion	3	3			
Cross Hatch Adhesion	3	3			
Humidity Resistance; Blistering, X-hatch, Pencil	3	3			
Neutral Salt Spray B 117	3		3	3	3

At the request of OO-ALC, adhesion properties will be evaluated after ASTM B 117 salt-fog exposure. Control System B and Mg-rich System G from TABLE 2 will have PATTI adhesion measurements performed after 2,000 and 3,000 hours of B 117 exposure. The measurements will be run in triplicate on unscribed panels.

### SUMMARY AND CONCLUSIONS

The ability to use cathodic protection as the primary mechanism to control the corrosion of aerospace aluminum alloys has been proven through the use of Mg-rich primers. This approach has shown to be particularly effective as part of a completely chromate free coating system. The most consistent positive performance has come thus far from the use of Mg-rich primer in combination with a non film forming surface treatment, such as PreKote™, and an APC grade topcoat. Non film forming surface treatments allow the aluminum substrate to electrically interact with the magnesium in the primer more effectively. APC grade topcoats provide enhanced electrolyte barrier properties which serve to both protect the aluminum substrate as well as the magnesium pigment present in the primer. Early prototype films of Mg-rich primer showed significant promise, however further modifications to the formulation was required in order to make a primer which had all of the desired properties for DoD aerospace applications. Despite initial concerns regarding the reactivity of magnesium metal pigment being used, the flammability and handling characteristics have not shown any potential problems to date.

The amount of testing required to transition a new class of corrosion protective primer coating such as this requires additional scope beyond that found in MIL-PRF-23377J. The current plan for transitioning the Mg-rich primer involves qualification to a "system level" coating specification, MIL-PRF-32239, for systems specific to those aircraft targeted for field demonstration. In addition, simulated lap joints with various fasteners specific to the target aircraft will be evaluated along with alternative substrates and reparability of the Mg-rich coating system. Finally, outdoor exposure testing will continue at Daytona Beach, FL for a minimum of one year. Four months of exposure have been completed to date with no evidence of corrosion.

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